STATE OF ILLINOIS
DEPARTMENT OF REGISTRATION AND EDUCATION

WETTABILITY OF COAL, GRAPHITE, AND NAPHTHALENE AS MEASURED BY CONTACT ANGLES

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ILLINOIS STATE GEOLOGICAL SURVEY
URBANA

1962

CIRCULAR 333

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ABSTRACT

Recent studies of contact angles on substances other than coal have indicated that comparison of angles formed by a liquid series on banded ingredients from coals of different rank might prove of value in research on Illinois coal and its utilization. Studies of the contact angles displayed by such a liquid series have allowed an estimate of both the free energy of the solid surface and its polar nature for surfaces of polymers, organic crystals, adsorbed monolayers, and several naturally occurring materials.

A method was developed for measuring advancing and receding contact angles on freshly exposed surfaces of small particles of coal. This method consisted essentially of measuring the contact angle between liquid and solid by inserting a small particle of the solid into the liquid surface in a controlled manner and measuring the angle between the profile of the solid surface and that of the liquid drop at their point of contact. Both advancing and receding contact angles were measured using this method for a series of liquids on naphthalene, graphite, a fusain from one coal, and a series of coal vitrains.

Plots of the cosine of the contact angle (θ) versus liquid surface tension (γ_L) indicated a linear relationship similar to that found for polymers, starch, and other surfaces of low, free energy (Ray et al., 1958; Scholz et al., 1958). Contact angle hysteresis was found to be quite large on the coal banded ingredients tested.

The cosine of the advancing contact angle displayed by a given liquid appeared to show a generally linear increase with decrease in rank (percent carbon in the coal). This was particularly true of water contact angles. Receding angles did not show this relationship. While physical surface structure as well as possibility of adsorption complicated the analysis, this was thought to be due to the increase in concentration of polar groups with decrease in rank of the coal.

INTRODUCTION

Wettability of a solid surface by a liquid can be most easily pictured in terms of the contact angle. If the angle between the solid and liquid surfaces as measured through the liquid is small, the wettability of the surface is rather large. Conversely, a large angle indicates that the solid surface is relatively less wettable insofar as the given liquid is concerned.

Contact angles measured on coal in the past have been primarily those of water and certain industrial oils. Recent information arising from studies of liquid contact angles on solid surfaces, however, has indicated that measurement of contact angles on banded ingredients of coal using liquids other than the above might prove of value. Knowledge of the magnitude of the contact angle of each of a series of pure liquids on a given solid surface allows a more fundamental understanding of the surface factors involved. Among possible benefits to be derived from following such a course of investigation might be the following:

1. The data would allow a better understanding of the effect of the surface nature of coal banded ingredients in coal cleaning.
2. Since knowledge of the magnitude of the contact angle is of direct application in froth flotation, determination of the type surface forces should allow more efficient selection of collectors, frothers, and modifying agents (Wark, 1938; Gaudin, 1939).
3. Information concerning variation in contact angles with liquid surface tension and with type of liquid should prove of value both in removing liquids from coal surfaces and in treating coal surfaces either for their protection or to prevent dust (Bailey and Gray, 1958; Brown et al., 1958).
4. Such data should allow a better application of theories of adhesion in predicting strength of coke.
5. Wettability data should be of assistance in blending inert materials with coals for production of coke.

A large number of contact angle measurements using various liquids on a great many surfaces of low free energy (primarily surfaces of polymers, monolayers, and organic crystals) have shown for a given solid surface a general, empirical, linear relationship between the cosine of the contact angle (Θ) and the surface tension of the liquid (γ_L). This linear relationship was especially evident in homologous series of liquids. The intercept of the line of best fit of the data with the line where cos Θ equals one on a plot of cos Θ vs. γ_L has been designated by Fox and Zisman (1950, 1952) as the critical surface tension (γ_C) for the particular liquid series and solid surface (see fig. 1). The surface tension of the solid (γ_S) easily can be demonstrated to be at least as high as the highest γ_C for advancing contact angles of any homologous series of liquids on this solid surface. Other investigation has also shown the γ_S as a rule should not be too much higher than γ_C (Good and Girifalco, 1960; Eissler, 1960).

A theory has been proposed which attempts to account for the interfacial energy between two liquid phases in terms of the magnitudes of surface energies of the individual phases (Girifalco and Good, 1957). This theory has now been extended (Good and Girifalco, 1960; Eissler, 1960) to account for relative magnitudes of contact angles of a liquid series on a solid surface. A function is defined.

$$\Phi = \frac{\Delta F^{a}_{ab}}{(\Delta F^{c}_{a})^{\frac{1}{2}}(\Delta F^{c}_{b})^{\frac{1}{2}}} \qquad 1)$$

where ΔF^{a}_{ab} is the work of adhesion between two phases and ΔF^{c}_{a} and ΔF^{c}_{b} are the works of cohesion within the phases. This function is defined as it is because a function of this form appears to relate empirically the attractive forces between unlike molecules to those between like molecules. A similar relationship (Berthelot, 1898) was defined to account for attractive force constants in the van der Waal equation. More recently, relationships of this form have been used to account for attraction between molecules having intermolecular forces which can be accounted for by either Lennard-Jones or Stockmayer potential functions (Hirschfelder et al., 1954). In these latter cases the functional form can be justified at least partially from quantum mechanical derivation.

The function, Φ , which can be related to the intermolecular forces and molecular geometries involved, will be equal to unity in the ideal case while its value will be greater or less than (usually less than) one in nonideal cases. More specifically, in cases where the liquid and solid are nonpolar* to the point where other type forces can be ignored and where molecular geometries within each of the phases are identical, then, in the absence of contact angle hysteresis, Φ will equal unity. In the case of a polar liquid and a nonpolar solid, however, or vice versa, Φ will be less than one.

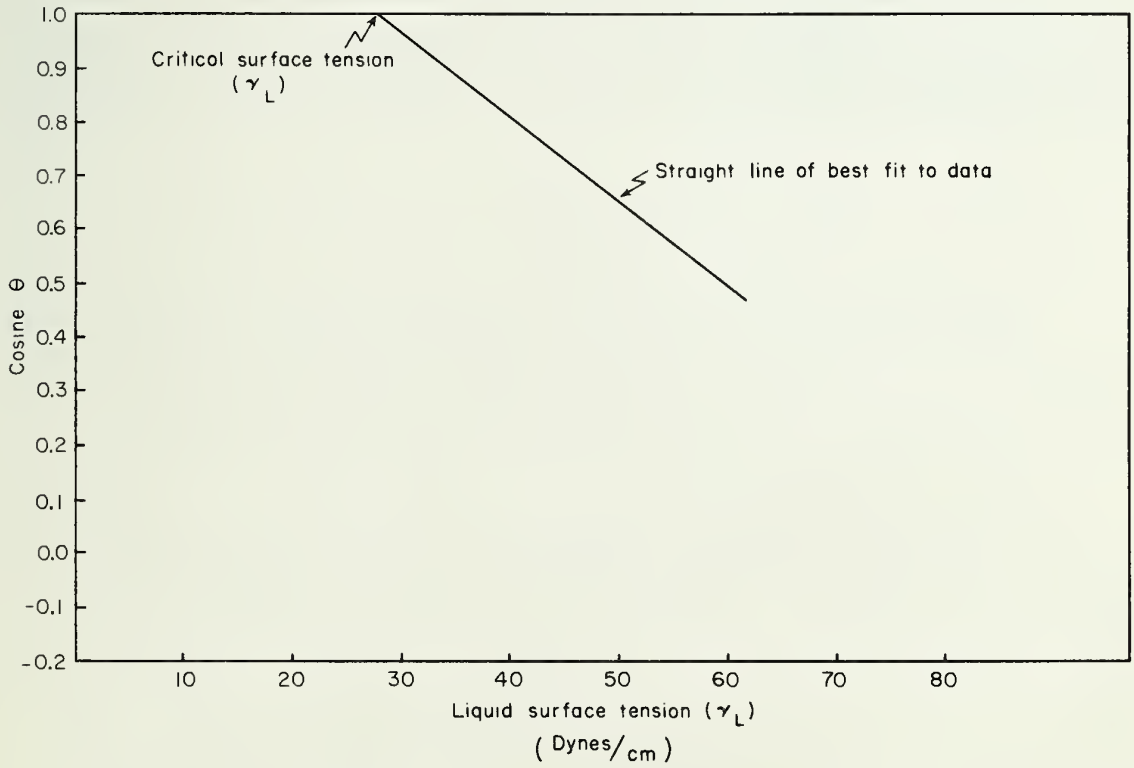

Fig. 1 - Illustration of the critical surface tension (γ_c).

The function, Φ, is also related to the contact angle by the equation

$$\text{Cos } \Theta = 2\Phi\gamma_S^{\frac{1}{2}}\left(\frac{1}{\gamma_L}\right)^{\frac{1}{2}} - 1 \qquad 2)$$

Evaluation of Φ by means of equation 2) requires a knowledge of the solid surface tension γ_S. If γ_S is considered to be independent of the liquid, however, ratios of Φ values of various liquids on a given solid surface are easily obtained from equation 3)

$$\frac{\Phi_2}{\Phi_1} = \frac{\gamma_{L_2}^{\frac{1}{2}}(\text{Cos } \Theta_2 + 1)}{\gamma_{L_1}^{\frac{1}{2}}(\text{Cos } \Theta_1 + 1)} \qquad 3)$$

where subscripts 1 and 2 refer to the two liquids being compared. Indeed, determination of Φ ratios for a series of liquids on a given solid surface in some cases will allow estimation of γ_S for the solid as well as individual Φ values. A method of estimation has been worked out for cases where nonpolar liquids having symmetrical molecules of relatively simple geometry can be used to measure contact angles on nonpolar solids (Eissler, 1960).

The Φ function has proved useful also in explaining the general empirical relationship between the cosine of the contact angle and liquid surface tension, as well as in estimating the relative polar-nonpolar nature of a solid surface. From the data presented in this publication, an attempt will be made to deduce at least semiquantitative information about the solid surfaces on which contact angles were measured.

TABLE 1 - IDENTIFICATION OF VITRAINS

Coal from which Vitrain was obtained	Vitrain specimen Designation
Pocahontas No. 4 (West Virginia)	A
Jewell (Virginia)	B
Eagle (West Virginia)	C
Illinois No. 5	D
Illinois No. 6 (Bituminous B)	E
Illinois No. 6 (Bituminous C)	F

PROCEDURE

Materials

Vitrains were selected from coals that spanned in rank the range of coking coals. Sources of vitrains and specimen designations are shown in table 1. Contact angles were also measured on one fusain and on faces and edges of graphite leaflets and naphthalene crystals. Vitrain specimens were broken from lumps of the whole coal, while the fusain was obtained from a 28 x 150 mesh fraction of the

*Polar type intermolecular forces are those which arise due to the interaction between permanent dipoles or between permanent dipoles and induced dipoles. Nonpolar type intermolecular forces are the result of induced dipole-induced dipole interactions. Molecules which possess permanent dipoles are said to be polar molecules. In addition to polar and nonpolar molecules, it is often the practice to speak of polar and nonpolar groups because, in general, one value of dipole moment is associated with the unsymmetrical occurrence of a given group in a molecule. An alkyl radical, for example, is generally regarded as a nonpolar, although it has a small polarity. However, -OH, -CN, -COOH, $-NO_2$, etc., are said to be polar groups because they are capable of contributing a relatively large value of dipole moment to a molecule.

TABLE 2 - SURFACE TENSIONS OF WATER AND ORGANIC LIQUIDS

Temperature = 20° ±0.5°C	
Liquid	Surface tension (dynes/cm)
Water	72.6
Glycerol	63.7
Formamide	58.7
Thiodiglycol	52.8
Ethylene glycol	47.6

material which had originally been taken from lenses occurring in the same coal seam as vitrain specimen E. The graphite was a natural Ceylon graphite which had been de-ashed, and the naphthalene was obtained by recrystallizing a technical grade of the material from alcohol solution.

The water used for contact angle measurements had been twice distilled. Organic liquids, obtained in the best available grade, were treated with silica gel and then stored over this same material until used.

Measured surface tensions of the liquids are reported in table 2, while results from chemical analyses of the banded ingredients of the coals are given in tables 3 and 4.

Apparatus

Because of the porous and heterogeneous nature of coal and because of the danger of altering properties of the surface while polishing, it was necessary to find a method suitable for measuring contact angles on freshly exposed coal surfaces without altering them in any other way. Fortunately, vitrains tend to break in a conchoidal fracture, leaving a rather smooth surface. The surface exposed after breakage, however, usually presents too much curvature and frequently too small an area to allow determination of the contact angle by the sessile drop method. Accordingly, a method was devised which gave measured contact angles comparable for such substances as naphthalene, teflon, and polyethylene with angles measured by the sessile drop method on these same materials, and which used small particles (about 1 x .3 x .3 mm) of the solid.

Where Young's equation* holds, the "true" contact angle reflects only the intermolecular forces within and between the phases. This "true" contact angle, then, should be independent of orientation in space and of other factors which do not depend on intermolecular or interatomic forces. The contact angle which is observed, however, depends on such factors as the distortion of the liquid surface and the effect of surface roughness in hiding the angle of contact at the intersection of the solid and liquid surfaces.

If a particle of a solid is partially inserted into a drop of liquid, the "true" contact angle between solid and liquid will be the same as that which occurs when a drop of liquid is placed on a smooth, solid surface. To measure a reproducible angle which is comparable to that measured by the sessile drop method requires that the solid particle be inserted into the liquid drop in such a manner that the liquid surface is not so much distorted that the angle cannot be distinguished at the magnification used.

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*Young's equation: $\gamma_S = \gamma_{SL} + \gamma_L \cos \Theta$

where γ_S is the surface tension of the solid
γ_{SL} is the interfacial tension between solid and liquid
γ_L is the surface tension of the liquid
Θ is the contact angle

TABLE 3 - CHEMICAL ANALYSES OF COALS

Coal	Proximate Analysis	
	Volatile matter (d.a.f.)	Fixed carbon (d.a.f.)
Anthracite	3.8%	96.2%
Vitrain specimen A	18.7	81.3
Vitrain specimen B	22.9	77.1
Vitrain specimen C	33.2	66.8
Vitrain specimen D	36.8	63.2
Vitrain specimen E	38.4	61.6
Vitrain specimen F	40.1	59.9
Fusain	19.3	80.7

Coal	Ultimate Analysis						
	Moisture*	Ash*	Carbon†	Hydrogen†	Nitrogen†	Sulfur†	Oxygen†
Anthracite	1.25%	2.77%	96.47%	2.01%	0.27%	0.49%	0.76%
Vitrain specimen A	1.40	1.81	93.42	5.01	0.41	0.68	0.47
Vitrain specimen B	0.63	2.63	91.07	5.18	0.43	0.57	2.75
Vitrain specimen C	1.15	0.92	86.90	5.35	0.58	0.73	6.44
Vitrain specimen D	1.93	1.33	84.90	5.45	0.55	0.84	8.27
Vitrain specimen E	2.40	0.85	83.50	5.45	0.70	0.61	9.74
Vitrain specimen F	4.20	0.58	83.70	5.83	0.63	0.60	9.24
Fusain	1.01	13.60	89.97	2.78	0.25	1.64	5.39

* Result given in percent of coal, as received.
† Result given in percent of dry, ash-free coal.
Oxygen by difference.

TABLE 4 - VALUES OF Φ_L* FOR ADVANCING ANGLES OF THE SERIES OF POLAR LIQUIDS ON COALS, NAPHTHALENE, AND GRAPHITE

Liquid	Naphthalene face	Naphthalene edge	Graphite face	Graphite edge	Anthracite
Water	0.809	0.867	0.698	0.791	0.723
Glycerol	0.875	1.029	0.757	0.869	0.847
Formamide	0.890	0.884	0.796	0.947	0.893
Thiodiglycol	—	—	0.900	0.949	0.933
Ethylene glycol	0.996	1.081	—	—	—

Liquid	Vitrain specimens						
	A	B	C	D	E	F	Fusain
Water	0.758	0.823	0.803	0.888	0.834	0.985	0.747
Glycerol	0.853	0.907	0.916	0.925	0.951	0.961	0.907
Formamide	0.907	0.931	0.933	0.955	0.964	0.980	0.970
Thiodiglycol	0.954	0.968	0.979	—	—	—	0.991

* Φ_L values were computed by use of the approximation $\gamma_S = \gamma_C$.

TABLE 5 - CONTACT ANGLES OF VARIOUS LIQUIDS ON GRAPHITE AND NAPHTHALENE

Liquid	Graphite faces		Graphite edges	
	θ_A*	θ_R†	θ_A	θ_R
Water	86.6°	67.7°	71.5°	60.9°
Glycerol	77.8	59.6	61.3	51.4
Formamide	60.7	47.4	46.5	41.8
Thiodiglycol	52.4	35.5	39.2	32.0

Liquid	Naphthalene faces		Naphthalene edges		(Sessile drop) Naphthalene edges	
	θ_A	θ_R	θ_A	θ_R	θ_A	θ_R
Water	91.8°	76.5°	95.8°	65.5°	90.8°	81.5°
Glycerol	81.1	69.0	82.0	52.2	82.7	71.5
Formamide	76.8	62.0	88.9	53.8	79.5	67.3
Ethylene glycol	59.3	50.5	67.4	46.8	59.8	51.9

*θ_A refers to the advancing contact angle.

†θ_R refers to the receding contact angle.

TABLE 6 - CONTACT ANGLES MEASURED ON COALS

Liquid	Coal surface							
	Anthracite		Vitrain specimen A		Vitrain specimen B		Vitrain specimen C	
	θ_A	θ_R	θ_A	θ_R	θ_A	θ_R	θ_A	θ_R
Water	85.5°	35.0°	80.1°	46.7°	73.8°	32.1°	75.0°	34.0°
Glycerol	69.8	27.8	65.8	34.6	60.3	20.1	52.2	20.8
Formamide	60.9	26.7	55.8	27.1	52.0	23.1	38.5	13.9
Thiodiglycol	51.3	20.3	48.4	12.4	41.5	21.0	27.1	11.0

Liquid	Coal surface							
	Vitrain specimen D		Vitrain specimen E		Vitrain specimen F		Fusain	
	θ_A	θ_R	θ_A	θ_R	θ_A	θ_R	θ_A	θ_R
Water	65.8°	23.8°	64.4°	26.4°	43.6°	0	74.2°	48.5°
Glycerol	50.7	13.8	41.4	15.2	37.7	0	47.5	28.3
Formamide	42.8	18.1	29.6	8.8	18.2	0	30.7	13.0
Thiodiglycol	very small	0	very small	0	0	0	9.5	6.3

For the series of experiments described here, two different versions of the same basic apparatus were developed (figs. 2 and 3). Each of these allowed inserting a solid particle into a drop of liquid in a controlled manner. The contact angle was then measured as the angle between the profile of the liquid surface and that of the solid surface at the point of their intersection. For observation of the angle, magnifications of about 300X were used. In principle it should have made no difference whether the particle had been inserted from below into a hanging drop or from above into a standing one. However, at magnifications of around 130X the former procedure caused many receding angles to be extremely difficult to measure.

In all cases reported here, contact angles were observed and measured using a microscope equipped with a goniometer eyepiece. All measurements were carried out at 20.0 $\pm$ 0.5 °C in a controlled temperature room.

Preparation of Specimens

All of the metal tools used for handling or breaking specimens were stored with the working ends immersed in ethylene dichloride. This liquid was removed by evaporation immediately before using the tool. All specimens were broken or cut while positioned on microscope slides. These slides had previously been cleaned with chromic acid cleaning solution, then rinsed with distilled water and dried. After drying, slides were stored under ethylene dichloride which was removed by evaporation immediately before they were used. Each slide was used only once before being recleaned.

As nearly as possible, contact angles were measured on freshly exposed, natural surfaces of coal. Larger lumps of coal were rebroken along vitrain bands with a hammer and chisel. Smaller pieces were chipped out of bands with the point of a knife and then were rebroken to suitable size. These small bits of coal were inspected under a binocular microscope, and pieces with surfaces as flat and smooth as possible were selected as specimens. Where coals were obtained in smaller sizes, pieces of vitrain could be recognized by their black, shiny surfaces. These pieces were fractured again with a knife and trimmed as described above.

The fusain had a more or less natural breakage which gave pieces of about 0.05 x 0.05 x 2.0 mm. Pieces which, on inspection under the binocular microscope, appeared to have smooth faces were mounted while being held between microscope slides.

All specimens were attached to the particle holder of the apparatus with celluloid cement and were used immediately after mounting. None of the solid surfaces appeared unstable with respect to any of the liquids, but no specimens were reused because one could not be certain of recleaning the surfaces.

Samples of coal were prepared for proximate analysis (macro) by first breaking the vitrain or fusain and then picking out all the mineral inclusions visible to the naked eye under a bright light. Samples were prepared for ultimate analysis (micro) by rebreaking the vitrain or fusain and picking out all the inclusions visible under a binocular microscope. Twenty-gram samples were prepared for the proximate analysis and 25- to 50-milligram samples were prepared for the ultimate analysis.

Determination of Liquid Surface Tension

Liquid surface tensions were measured by a variation of the capillary rise method. Apparatus and method have been described by Natelson and Pearl (1935). Measurement of surface tension involved determining the rise of liquid in a small-bore capillary tube when this rise was opposed by the usual gravitational forces as well as the force created by a meniscus in a capillary tube of larger bore.

Technique Used to Measure Contact Angles

Contact angle measurements were taken in an atmosphere exposed to the equilibrium vapor pressure of the liquid. Small drops of liquid were placed inside the cell (A) (see figs. 2 and 3) which also contained the solid specimen (B) and the drop of liquid (C) used for measuring the contact angle. The system was then allowed to equilibrate before readings were taken. All data reported here were measured by inserting the solid particle into the standing drop from above, with the profile of the surface of the solid as nearly vertical as possible.

To center the liquid drop, the vertical cross-hair of the goniometer eyepiece (K) was first aligned with the profile of the solid surface on which the contact angle was to be measured. After alignment the liquid drop was centered on the cross-hair by means of a sliding block mechanism (D). The particle was inserted into and withdrawn from the liquid drop by adjusting a micrometer screw (E) which moved a spring-loaded, 1 mm diameter shaft (F). To the end of this shaft was affixed the specimen holder (H) in one version of the apparatus and the drop holder (G) in the other version. The rotation necessary to align the profile of the solid surface was accomplished by rotating the entire micrometer and rod assembly (I) in both versions of the apparatus.

To use the apparatus the equilibrating liquid was first placed in the chamber after which the specimen, previously mounted on a specimen holder, was attached. The drop holder (G), previously cleaned, was placed in the apparatus and the drop was placed on its teflon surface by forcing liquid from a fine glass capillary tube with an eyedropper bulb. In the first apparatus (fig. 2) this was followed by aligning the specimen. In the second apparatus (fig. 3) the cover (J) was first placed on the apparatus after which the specimen was aligned. For all liquids except water a 15-minute equilibration time was allowed after attaching the cover before readings were taken.

Drops of liquid were transferred by means of fine capillaries drawn from glass tubing. In every case at least 5 cm of the end of the capillary was broken off with clean tweezers before use. Each capillary tube was used only once.

The solid specimen was positioned in such a manner that the profile of the surface on which the contact angle was to be measured was precisely placed over the center of the drop. Angles were measured in the plane of the drop profile. This was accomplished by focusing the microscope back and forth through the drop until the profile was in sharpest focus. To measure the contact angle, the cross-hair of the eyepiece was first aligned with the profile of the solid surface and the position of the cross-hair determined by reading the goniometer scale. The eyepiece was then rotated until the cross-hair was tangent to the profile of the drop at the point of intersection of drop and solid surface and the position of the cross-hair was again determined. The difference between these readings was the contact angle.

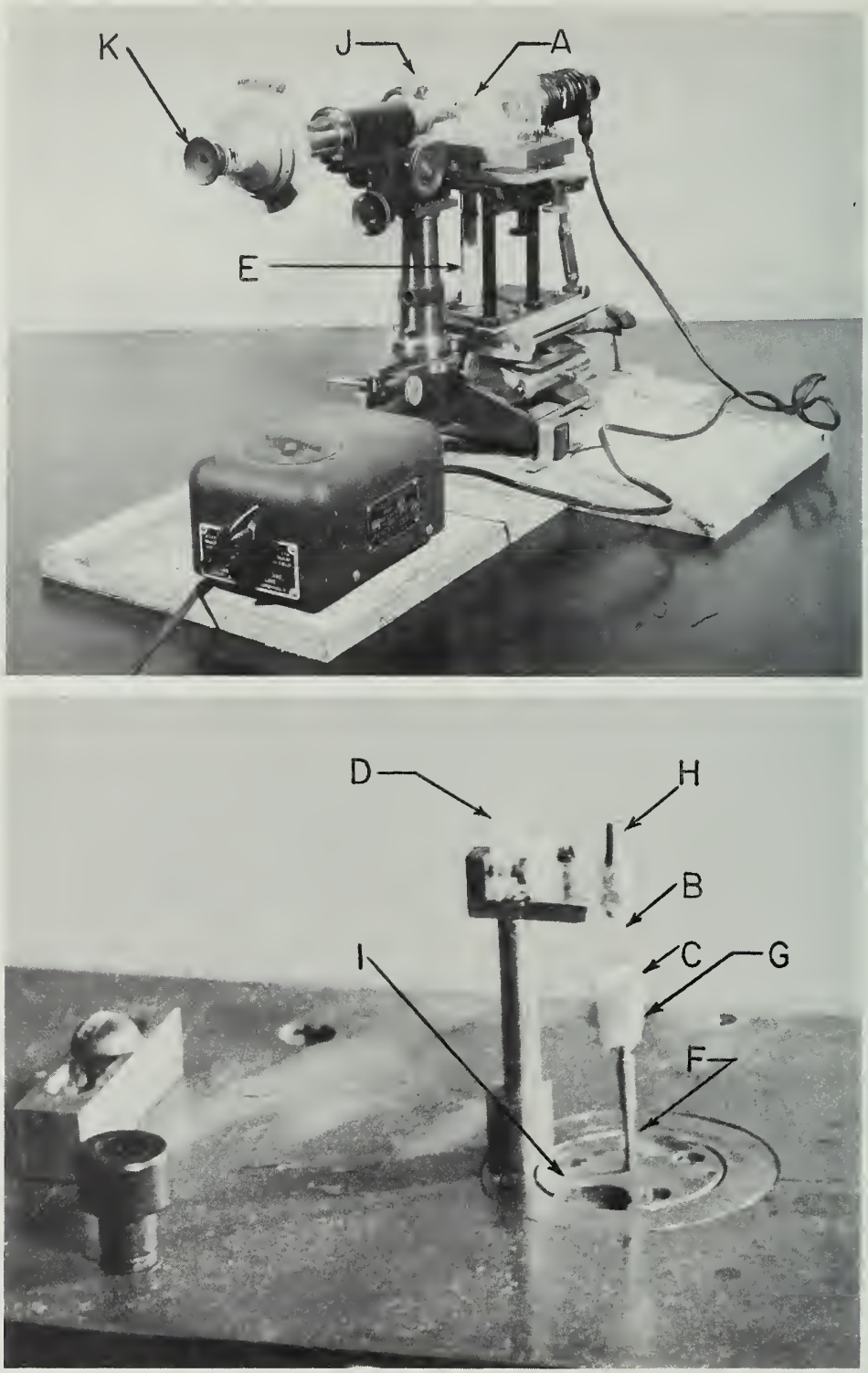

Fig. 2 - Apparatus for measuring contact angles.

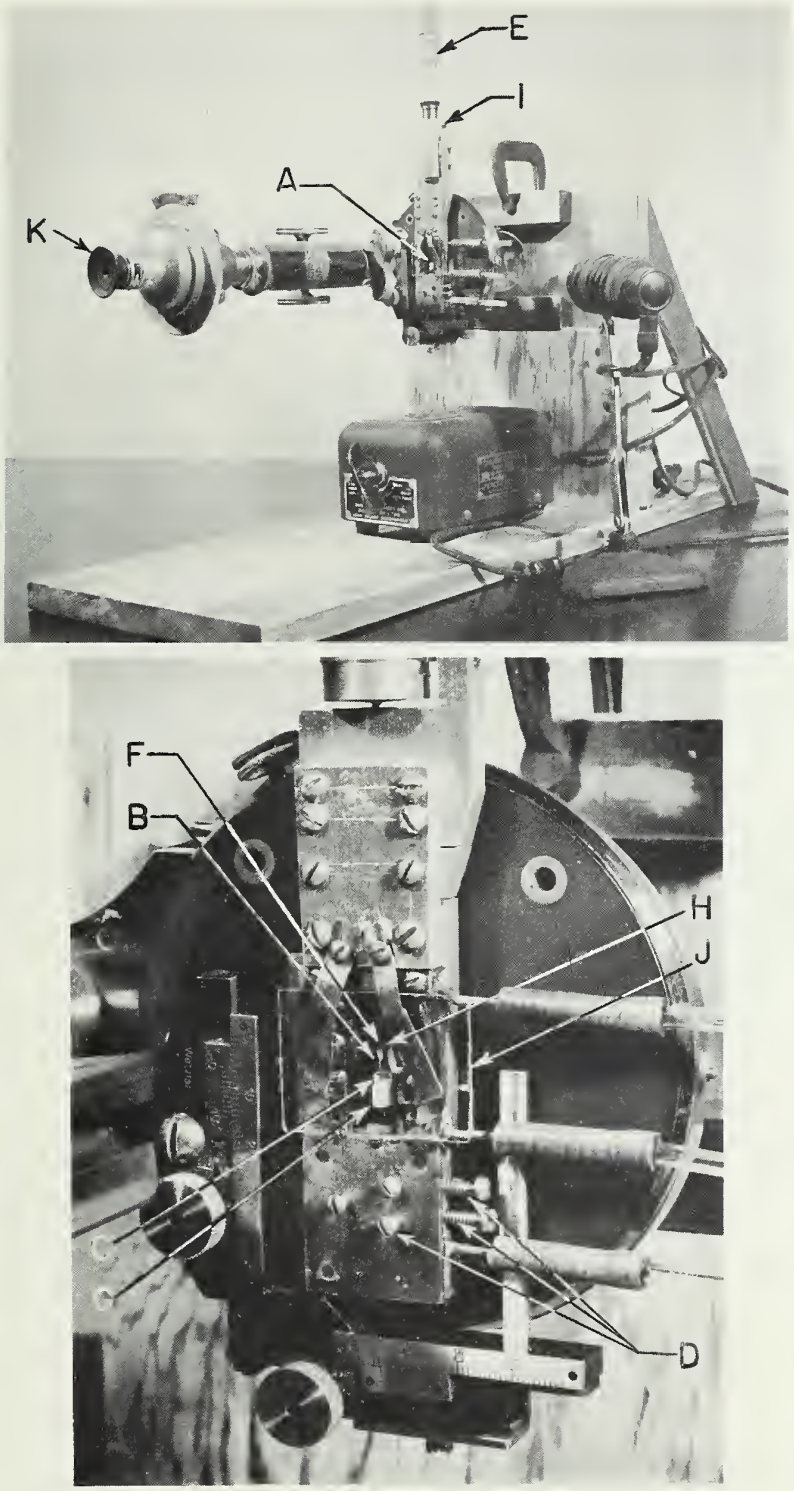

Fig. 3 - Miniaturized apparatus for measuring contact angles.

Advancing angles were formed by inserting the particle into the drop with the micrometer screw until the liquid was observed to just advance over the solid. Receding angles were formed by withdrawing the particle from the drop until the liquid was observed to just recede. Contact angles of all liquids except water were measured one minute after advancing or receding the liquid. With water, where some difficulty was encountered because of evaporation of the drop, 20 seconds were allowed before measuring the angle.

Advancing and receding angles reported are each the average of at least six measurements. Generally three advancing and three receding angles were measured on each of two specimens. Usually the liquid was advanced to a position for an observation and allowed to stand for one minute, after which an advancing angle was measured. The particle was then withdrawn until the liquid surface receded slightly and after a one-minute wait a receding angle was measured.

Because the natural surfaces of naphthalene, graphite, and the coals were less smooth than a polished surface would have been, a little more difficulty was encountered in finding the reproducible angle than would have been found on the latter type surface. Occasionally an angle was measured which varied as much as ±15° from the reproducible one. When such an angle was encountered, the liquid surface close to the point of measurement was observed to be unusually distorted. Very thin specimens of graphite failed to give reproducible contact angles for edges of the leaflets. This was apparently caused by a distortion of the drop surface because of the characteristic contact angle at the face of the leaflet. In any case, no nonreproducible angles are reported here on any surfaces.

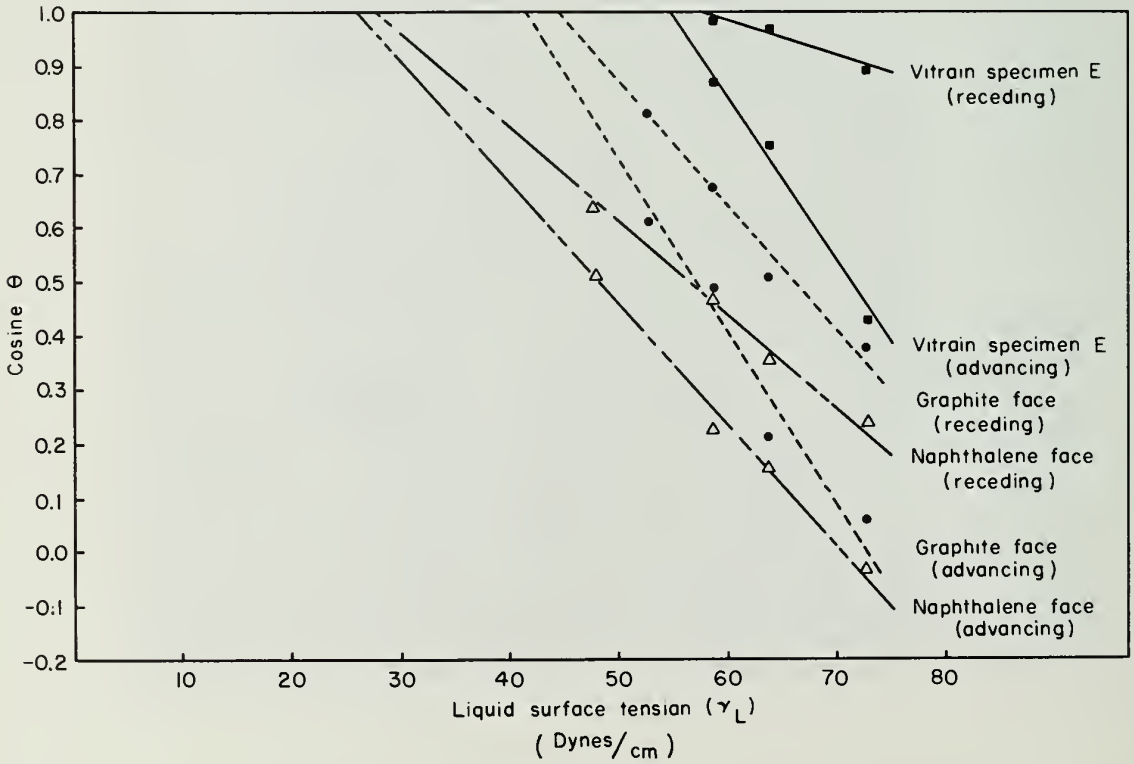

Fig. 4 - Illustration of typical fit of curves to data.

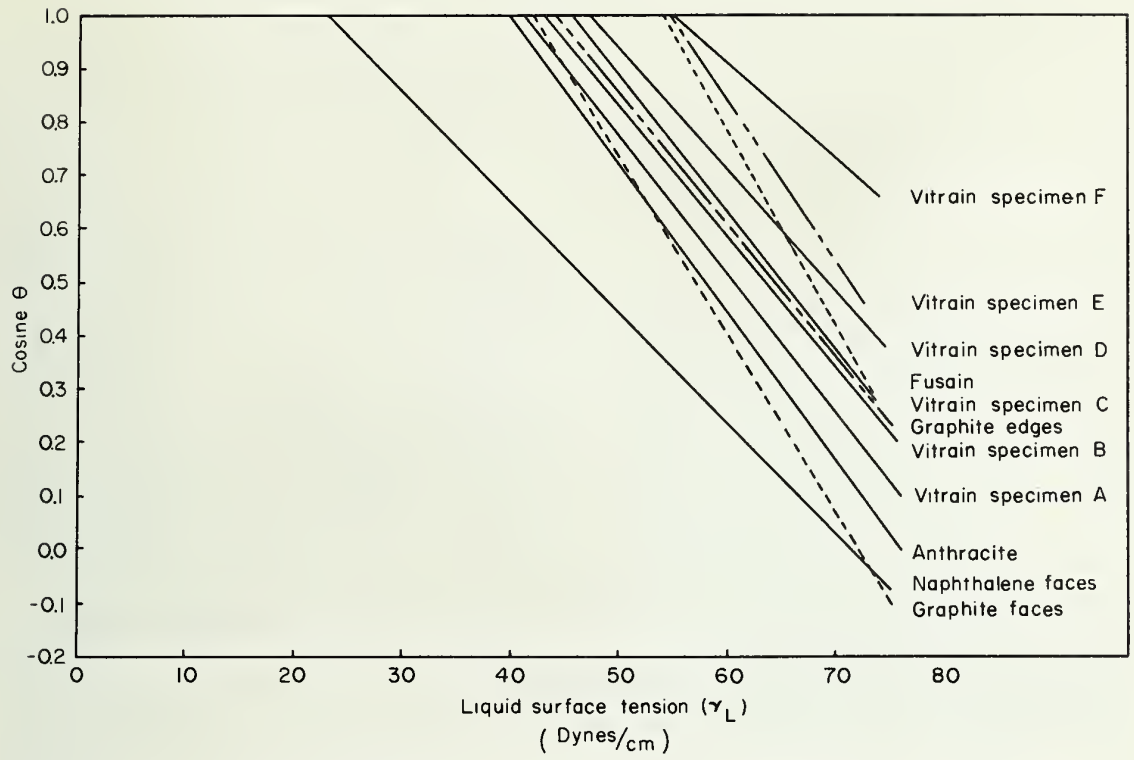

Fig. 5 - Composite-curves of advancing contact angles.

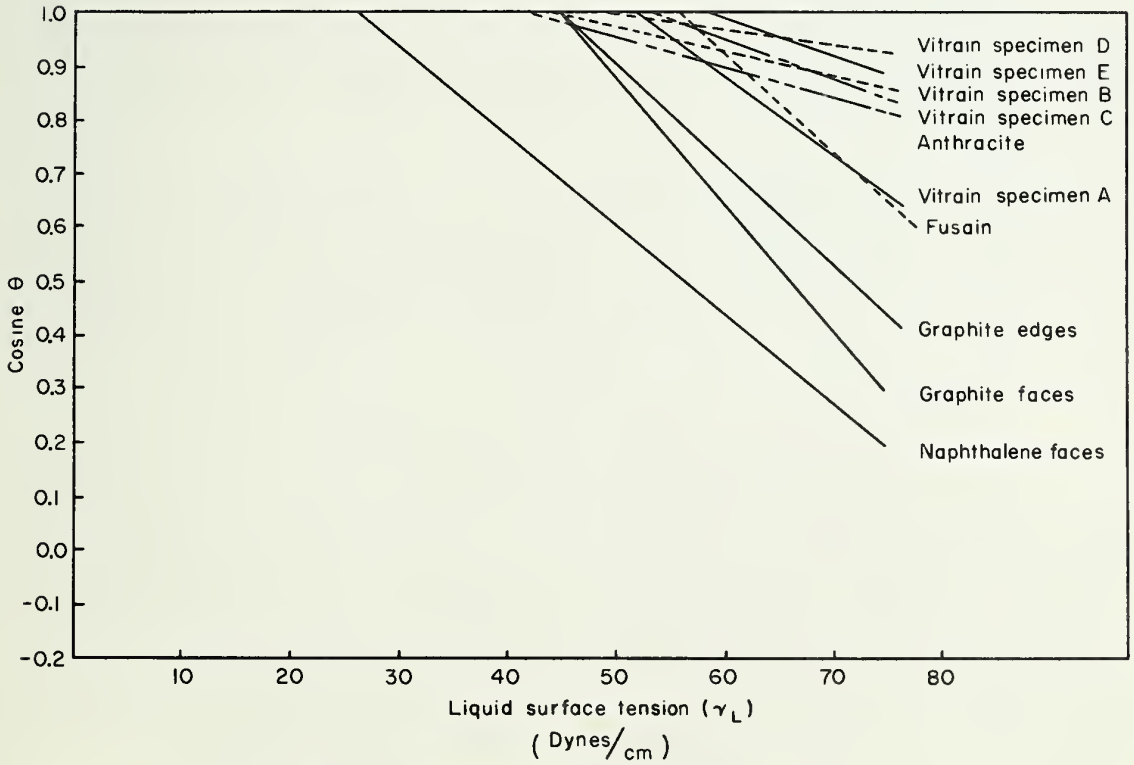

Fig. 6 - Composite-curves of receding contact angles.

RESULTS AND DISCUSSION

Measured values of advancing and receding angles are given in tables 5 and 6. The curves shown in figures 4, 5, and 6 are based on these data, and values of γ_C for advancing angles are presented in table 7.

TABLE 7 - VALUES OF γ_C FOR THE SERIES OF ADVANCING ANGLES OF POLAR LIQUIDS ON COALS, NAPHTHALENE, AND GRAPHITE

Surface	γ_C (dynes/cm)
Naphthalene face	23.0
Naphthalene edge	19.5
Graphite face	42.0
Graphite edge	44.0
Anthracite	39.8
Vitrain specimen A	41.0
Vitrain specimen B	43.0
Vitrain specimen C	50.5
Vitrain specimen D	47.3
Vitrain specimen E	54.7
Vitrain specimen F	56.0
Fusain	54.0

Unfortunately, the coal surfaces used in this investigation all proved to be of sufficiently high free energy that all liquids showing a non-zero contact angle were of a highly polar and associated nature. This prevented any estimation of γ_S or of individual Φ values based on parameters from potential functions such as that which had been carried out for nonpolar liquids on nonpolar solid surfaces (Eissler, 1960). Because of the very polar nature of all of the liquids, it also was not possible to compare variation in Φ value with liquid polarity on any given surface. It was possible, however, by use of the approximation, $\gamma_S \approx \gamma_C$, to estimate semi-quantitatively by use of Φ values, the comparative polar nature of the solid surfaces.

Plots of cos Θ vs. γ_L (figs. 4, 5, and 6) showed a surprising linearity for all of the coal surfaces as well as for those of naphthalene and graphite. This same linearity had been noticed by other investigators for similar plots of contact angle data measured on surfaces of starch and cellulose which are, like coal, rather complex, naturally-occurring materials. Available literature appears to bear out the fact that contact angle hysteresis, at least of water, is quite large on coals.

The plot of cos Θ vs. percent carbon for water and glycerol advancing contact angles (fig. 7) of graphite, vitrains, and the fusain indicates a more or less steady increase in magnitude of cos Θ with decrease in rank of the coal. The surfaces badly out of line are those of vitrain specimen F, which was a high-moisture coal, and the edges of graphite leaflets. Vacuum drying of the B and E vitrain specimens, however, followed by measurement of the glycerol contact angle in a dry nitrogen atmosphere showed no change, within experimental error, for either of these surfaces.

The linear relationship between cos Θ and percent carbon also holds true for other liquids on vitrain surfaces, but those of fusain and, to a lesser extent, of graphite are sufficiently more wettable by lower surface tension liquids to make them anomalous. This linear relationship also does not hold for receding contact angles in general. A plot of cos Θ vs. percent carbon for receding contact angles indicates a minimum, with the exception of the vitrain specimen B, at a carbon content of around 90 percent. While bubble contact angles, especially on porous materials, are strictly comparable with neither advancing nor receding angles measured by the method used in this study, it is interesting to note that data by Horsely and Smith (1951) taken by the former method on a series of coals also indicated a maximum contact angle at about 90 percent carbon.

By use of the approximation, $\gamma_S \approx \gamma_C$, Φ_L can be estimated from the equation

$$\Phi_L = \frac{\gamma_L^{\frac{1}{2}}(\cos\Theta+1)}{2\gamma_C^{\frac{1}{2}}} \qquad 4)$$

Table 4 presents Φ_L values computed in this manner for advancing contact angles on the solid surfaces. Figure 8 is a plot of Φ_L vs. percent carbon for graphite and coal surfaces. It should be noted that, since only advancing angles are being compared here, there is a component due to contact angle hysteresis in these data as well as that due to strictly polar-nonpolar nature of the solid surfaces.

Computed from advancing angles, water displays a range of Φ_L values of from 0.98 for the surface of vitrain specimen F to 0.72 for that of anthracite, while formamide shows values of 0.98 and 0.89 respectively on these same two surfaces. The difference in Φ_L values for water and formamide is probably in a large part due to the effect of contact angle hysteresis.

It should be noted that a rather large increase in γ_S over that used in making the estimate in the above cases would not change the estimated Φ_L proportionately. For example, changing the estimate of γ_S for graphite from 48 dynes/cm to 70 dynes/cm would change the value of Φ_L calculated for water on this surface from 0.70 to 0.54, and increasing the estimated γ_S for vitrain specimen A by 20 percent would change the value of Φ_L calculated for water on this surface from 0.76 to 0.69.

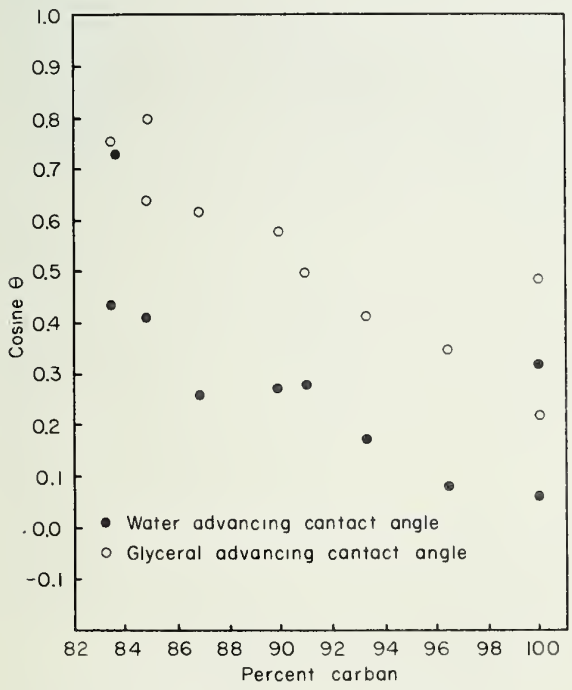

Fig. 7 - Trend of Cos Θ with carbon content for advancing contact angles of glycerol and water.

CONCLUSIONS

Ellison and Zisman (1954) have shown that to a first approximation the cosine of the contact angle of a given liquid on polymer surfaces composed of different mole fractions of methylene and CF_2 groups varies linearly with the mole fraction of the groups in the surface. They also demonstrated this to be true for polymer surfaces composed of different mole fractions of CF_2 and CCl_2 groups. If this were used as a general criterion, comparison of the curves for graphite, naphthalene, and the coals in figures 5 and 6, as well as data from other sources (Eissler, 1960) for surfaces composed of methyl and methylene groups, would indicate that aromatic and aliphatic structures alone could not account for wettabilities of surfaces of either vitrains or the fusain. In terms of functional groups, only the polar groups (see footnote on page 4), probably

primarily the oxygen groups, present in these surfaces could account for this increased wettability shown by the lower rank coals.

Physical surface structure as well as the possibility of adsorption complicate the analysis. Either porosity (Cassie and Baxter, 1944) or the presence of adsorption on the surface (Gregg, 1951) would decrease wettability. The density of the material would also affect wettability of the surface. Density of dry, ash-free coal, however, with the increase in rank of lower rank coals shows a small decrease to a minimum with coals of 88 percent carbon (Van Krevelen and Schuyer, 1957). Thereafter it increases rapidly through anthracite to graphite. This factor taken alone would mean an increase in wettability with rank in coals of above 88 percent carbon.

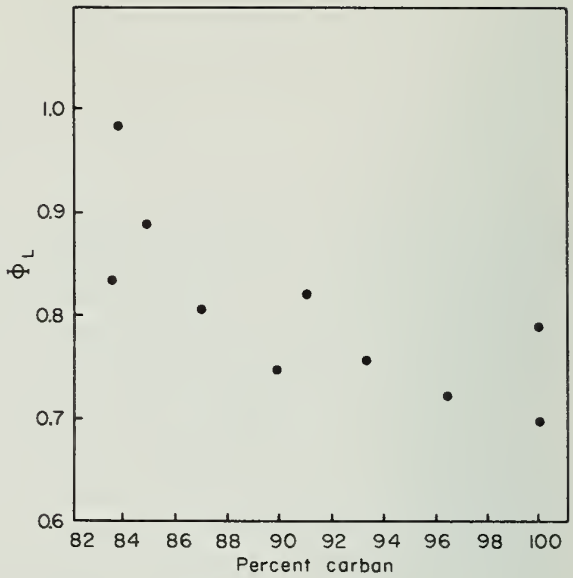

Fig. 8 - Trend of Φ_L values with carbon content for advancing contact angles of water.

The decreasing value of Φ_L for contact angles of polar liquids with increase in carbon content of vitrains and the fusain undoubtedly means a decreasing polarity of the surfaces with increasing rank. This would be due, most probably, to increase in concentration of the polar groups with decrease in rank of the coals.

In this study no applications of the concept of wettability to problems of coal beneficiation or utilization were attempted. The data presented here, however, do suggest avenues for application of contact angle research to practical problems in the coal industry. Operations where such data would be useful might include froth flotation, drying, dustproofing, and blending and carbonization of coals for coke.

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Illinois State Geological Survey Circular 333
20 p., 8 figs., 7 tables, 1962

Printed by Authority of State of Illinois, Ch. 127, IRS, Par. 58.25.

CIRCULAR 333

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